GREAT RIVER
ENERGY℠

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April 29, 1999

Mr. William Maxwell
Emission Measurement Center (MD-13)
U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

Attn: Electric Utility Steam Generating Unit Mercury Test Program

Dear Mr. Maxwell,

Great River Energy's Coal Creek Station (CCS) Unit 2 was selected by the Environmental Protection Agency (EPA) to perform speciated mercury emissions testing. The notification letter from Sally Shaver, EPA stated if the unit has been tested since January 1, 1996, and the following conditions are met, the owner/operator may elect to submit the report of that testing in lieu of conducting additional testing. CCS performed mercury speciation as part of the "Mercury Formation and Fate" study in August 1998. The study meets all the conditions required for the substituted test report to be accepted:

1. Use of "Standard Test Method for Elemental, Oxidized, Particle-bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).

   All methods and analytical procedures used to determine mercury speciation and chlorides in the flue gas, as well as the total mercury in the solid and liquid streams of the plant followed EPA Methods 1-4, 5,17, 29,and 26A.

2. Use of quality assurance/quality control procedures equivalent to those required in the QAPP.

   EERC has an overall QA/QC program to maintain overall data integrity. However, the following additional procedures were instituted specifically for this project:
   - Instrument Setup and Calibration
   - Presampling Preparation
   - Glassware and Plasticware Cleaning and Storage
   - Analytical Reagents
   - Blanks
   - Spiked Samples

   Details of the additional procedures can be found in the "Mercury Formation and Fate Report".

3. Use of the report format presented in the EPA document entitled "Preparation and Review of Emission Test Reports".

   The Mercury Formation and Fate Report is included.

Energy & Environmental Research Center

MERCURY SPECIATION SAMPLING AT COOPERATIVE AND UNITED POWER ASSOCIATIONS' COAL CREEK STATION

FINAL
~~Interim~~ Report

Prepared for:

Mr. Tom Brown

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Coal Creek #2
D-14
— Final Report (?) Data, Plant identified

November 1998

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ABBREVIATIONS

Al_2O_3	alumina (aluminum oxide)
ANSI	American National Standards Institute
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
Btu	British thermal unit
°C	degrees Celsius
CAAAs	Clean Air Act Amendments
CaO	calcium oxide
CEM	continuous emission monitor
Cl_2	chlorine gas
CO_2	carbon dioxide
CVAA	cold-vapor atomic absorption
DOE	U.S. Department of Energy
EERC	Energy & Environmental Research Center
EPA	U.S. Environmental Protection Agency
ESP	electrostatic precipitator
°F	degrees Fahrenheit
Fe_2O_3	iron(III) oxide
FGD	flue gas desulfurization
g	gram
H_2O_2	hydrogen peroxide
H_2SO_4	sulfuric acid
HCl	hydrogen chloride
HF	hydrofluoric acid
Hg	mercury
Hg^0	elemental mercury
Hg^{2+}	oxidized mercury
HNO_3	nitric acid
hr	hour
K_2O	potassium oxide
KCl	potassium chloride
klb	kilopound
kscfm	thousand standard cubic feet per minute
L	liter
lb	pound
MMBtu	million (10^6) British thermal units
mg	milligrams
MgO	magnesium oxide
min	minute
MW	megawatt
NA	not acceptable

ABBREVIATIONS (continued)

Na_2O	sodium oxide
NaOH	sodium hydroxide
ND	not detected
NIST	National Institute of Standards and Technology
nm	nanometer
Nm^3	normal cubic meter (20°C and 1 atmosphere)
NO_x	nitrogen oxides (nitric oxide and nitrogen dioxide)
O_2	oxygen
P_2O_5	phosphorus pentoxide
ppb	parts per billion
ppm	parts per million
psig	pounds per square inch gauge
QA	quality assurance
QC	quality control
scf	standard cubic feet
scfm	standard cubic feet per minute
SiO_2	silica (silicon dioxide)
SO_2	sulfur dioxide
SO_3	sulfur trioxide
Std. Dev.	standard deviation
TiO_2	titanium oxide
µg	micrograms
% $^V/_V$	percentage by volume
% $^W/_V$	percentage by weight

MERCURY SPECIATION SAMPLING AT COOPERATIVE AND UNITED POWER ASSOCIATIONS' COAL CREEK STATION

EXECUTIVE SUMMARY

1.0 INTRODUCTION

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. Two mercury reports to Congress were issued.[1] Given the current state of the art, these reports did not state that mercury controls on coal-fired electric power stations should be required. However, they did indicate that EPA views mercury as a potential threat to human health and additional research/information was necessary. To address the issue of mercury emissions and their impact on the Devils Lake area, a consortium was set up and a contract put in place with the Energy & Environmental Research Center (EERC). The purpose of the project was to measure speciated mercury emissions from two North Dakota plants and to determine the concentration of mercury in sediments in Devils Lake.

The consortium consisted of the following groups:

- Minnkota Power Cooperative, Inc., the owner and operator of the Milton R. Young Station, located near Center, North Dakota

- Cooperative Power Association, the owner and operator of the Coal Creek Station located near Underwood, North Dakota

- North Dakota Industrial Commission

- U.S. Department of Energy (DOE) through the Jointly Sponsored Research Program with the EERC

- EPRI

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[1]U.S. Environmental Protection Agency. Web site at http://www.epa.gov/airlinks/.

The project is divided into two tasks. Task 1 is focused on determining the abundance and forms of mercury emitted. Task 2 addresses discrepancies noted in the literature regarding the source of mercury in lakes. This report gives the results from the mercury sampling that was completed at the Coal Creek Station during the week of August 3, 1998.

2.0 OBJECTIVES

The four primary objectives of the Coal Creek Mercury Speciation Test Program (Task 1) are as follows:

- Determine the speciated mercury emissions from the station
- Use a continuous emissions monitor (CEM) to measure total mercury at the stack
- Provide electrostatic precipitator (ESP) and flue gas desulfurization (FGD) removal efficiencies for each the mercury species
- Calculate mercury material balances

3.0 APPROACH

Flue gas sampling at the Coal Creek Station's Unit 2 was completed to determine the mercury speciation at five different points in the system: at the air preheater inlet, inlet to one of the ESPs, outlet of the ESP/inlet to the FGD unit, outlet of the FGD unit, and the stack. All mercury speciation measurements were made using the Ontario Hydro method, which has been validated in pilot-scale tests at the EERC.[2] During the testing, the FGD system was operated with lime as the scrubbing medium.

3.1 Results

Figures ES-1 and ES-2 present graphically the results of the mercury sampling. These two figures show the change in mercury concentration and speciation across the ESP and FGD systems,

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[2] Laudal, D.L.; Heidt, M.K. *Evaluation of Flue Gas Mercury Speciation Methods*; EPRI Report No. TR-108988; Dec. 1997.

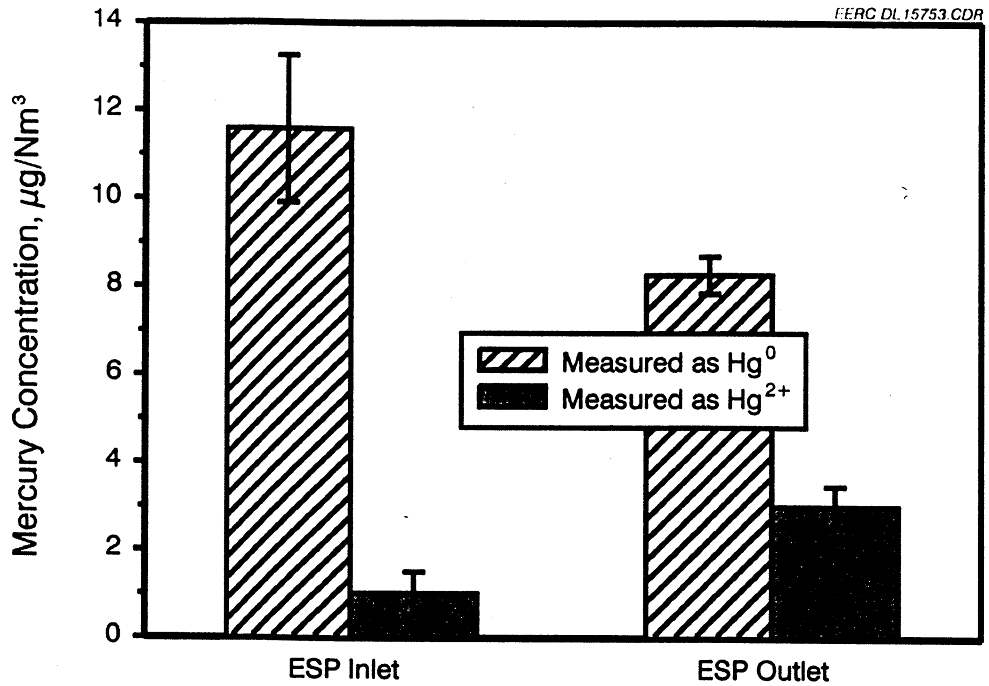

Figure ES-1. The change in vapor-phase speciated mercury across the ESP.

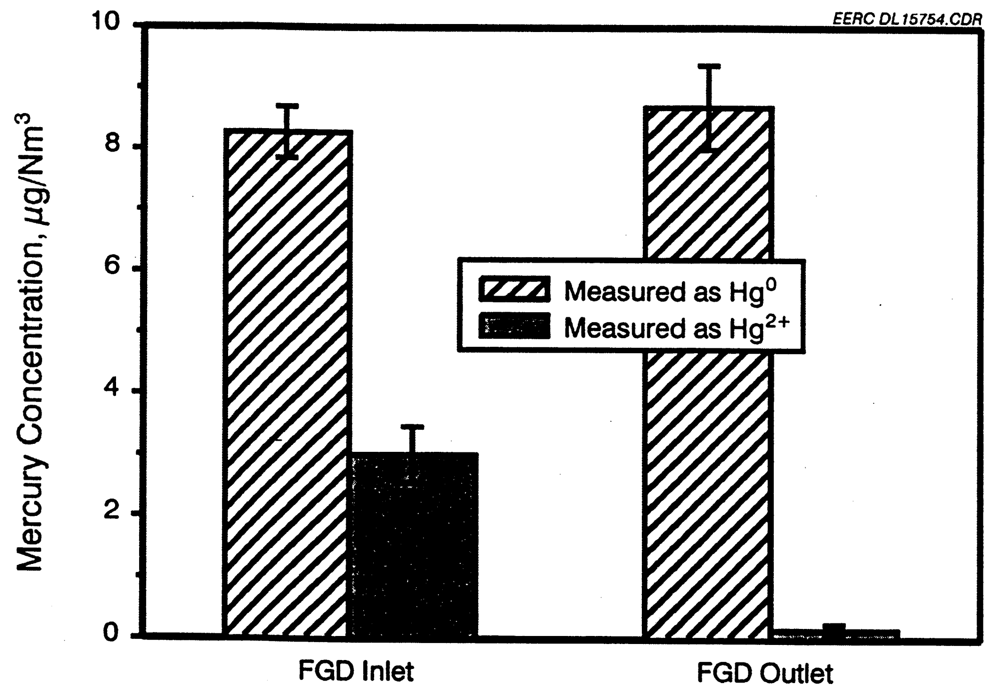

Figure ES-2. The change in vapor-phase speciated mercury across the FGD system.

respectively. A summary of the speciated mercury emission factors for Unit 2 at the Coal Creek Station is given in Table ES-1.

TABLE ES-1

Emission Factors for Mercury at Unit 2 Stack

Day	Hg^{2+}, lb/10^{12} Btu	Hg^0, lb/10^{12} Btu	Total Hg, lb/10^{12} Btu
1	0.88	8.42	9.31
2	0.93	8.41	9.34
3	0.67	6.78	7.44

3.2 Conclusions

The following conclusions were drawn from the results of the testing at the Coal Creek Station:

- The mercury at the FGD inlet was about 30% Hg^{2+} and 70% Hg^0.
- The FGD system removes almost all the Hg^{2+} but little if any Hg^0. However, at the stack the mercury emissions were about 15% Hg^{2+} because of the FGD bypass.
- Although little if any mercury was removed by the ESP, about 20% of the Hg^0 was converted to Hg^{2+} across the ESP.
- The Semtech Hg 2000 CEM gave total mercury results very comparable to those given by the Ontario Hydro mercury speciation sampling method.
- The mercury emission factor for Unit 2 of the Coal Creek Station averaged 8.57 ± 1.01 lb/10^{12} Btu.
- Excellent mercury balances were obtained around Unit 2, the ESP, and FGD systems.
- Almost 100% of the mercury captured by the scrubber was associated with the solid portion of the scrubber sludge.

MERCURY SPECIATION SAMPLING AT COOPERATIVE AND UNITED POWER ASSOCIATIONS' COAL CREEK STATION

1.0 INTRODUCTION

1.1 Test Program Background

The 1990 Clean Air Act Amendments (CAAAs) required the U.S. Environmental Protection Agency (EPA) to determine whether the presence of mercury in the stack emissions from fossil fuel-fired electric utility power plants poses an unacceptable public health risk. EPA's conclusions and recommendations were presented in the *Mercury Study Report to Congress* (1) and *Utility Air Toxics Report to Congress* (1). The first report addressed both the human health and environmental effects of anthropogenic mercury emissions, while the second addressed the risk to public health posed by the emission of mercury and other hazardous air pollutants from steam–electric generating units. Although these reports did not state that mercury controls on coal-fired electric power stations would be required given the current state of the art, they did indicate that EPA views mercury as a potential threat to human health. Therefore, it was concluded that mercury controls at some point may be necessary. EPA also indicated that additional research/information was necessary before any definitive statement could be made. This has led EPA to propose a controversial information collection request.

A consortium was set up to determine the speciation and levels of mercury emissions from North Dakota power plants and if these emissions impact the Devils Lake area. The Energy & Environmental Research Center (EERC) was contracted to measure mercury emissions from two North Dakota power plants and to determine the level of mercury in sediments in Devils Lake. The consortium consisted of the following groups.

- Cooperative Power Association, the owner (along with United Power Association) and operator of the Coal Creek Station located near Underwood, North Dakota
- Minnkota Power Cooperative, Inc., the owner and operator of the Milton R. Young Station, located near Center, North Dakota
- North Dakota Industrial Commission

- U.S. Department of Energy (DOE) through the Jointly Sponsored Research Program with the EERC

- EPRI

The project is divided into two tasks. Task 1 is focused on determining the abundance and forms of mercury emitted at two North Dakota utilities. Task 2 addresses discrepancies noted in the literature regarding the source of mercury in lakes. This report presents the results from the mercury sampling that was completed at the Coal Creek Station during the week of August 3, 1998.

1.2 Test Program Objectives for Task 1

The following objectives of the Coal Creek Mercury Speciation Test Program (Task 1) were accomplished:

- Determine the mercury emissions and speciation of the mercury emissions from the station

- Use a continuous emissions monitor (CEM) to measure total mercury at the stack

- Provide electrostatic precipitator (ESP) and flue gas desulfurization (FGD) removal efficiencies for each the mercury species

- Calculate mercury material balances

1.3 Sampling Approach

Table 1-1 identifies the mercury-sampling test program matrix. Representative samples were collected and analyzed for mercury from each of the targeted flue gas streams, two solid streams, and five FGD liquid/sludge streams.

2.0 TEST DESCRIPTION

This section describes the Coal Creek Station and the various sample locations that were used for the test program. The process operation during testing is also described.

TABLE 1-1

Mercury Speciation Test Program Matrix at Coal Creek Power Station

Process Stream	Target Mercury Species: Hg^0 (elemental)	Hg^{2+} (oxidized)	Total Hg
Flue Gas Sample Streams			
Air Preheater Inlet	X	X	X
ESP Inlet	X	X	X
ESP Outlet/ FGD Inlet	X	X	X
FGD Outlet	X	X	X
Stack	X	X	X
Solid Samples			
Coal feeders (composite of the feeders)			X
ESP Hoppers			X
Lime			X
Liquid Samples			
Lime Slurry			X
FGD Slurry			X
Scrubber Blowdown			X
Ash Sluice Water			X
Ash Pond Makeup Water			X

2.1 Unit Description

The Coal Creek Station is a minemouth electrical generating plant located about 50 miles north of Bismarck near Underwood, North Dakota. The plant, owned by Cooperative and United Power Associations of Minnesota and operated by Cooperative Power, supplies electricity for people in west central and southern Minnesota. The Coal Creek Station consists of two units. Unit 1, which began operating in 1979, has a capacity of 550 megawatts (MW). Unit 2, which also has a generating capacity of 550 MW, began operating in 1981. Both units are dry-bottom furnaces with a Combustion Engineering controlled circulation boiler. Originally, both units were tangentially fired boilers; however, during the summer of 1998, Unit 2 was converted to low-NO_x burners with overfire air. At full load, Unit 2 is designed to burn up to 560 tons of lignite per hour to produce 3,737,000 lb of steam at 2620 psig and 1005°F. All the mercury sampling completed for this project was done on Unit 2. A schematic of the Unit 2 system is shown in Figure 2-1.

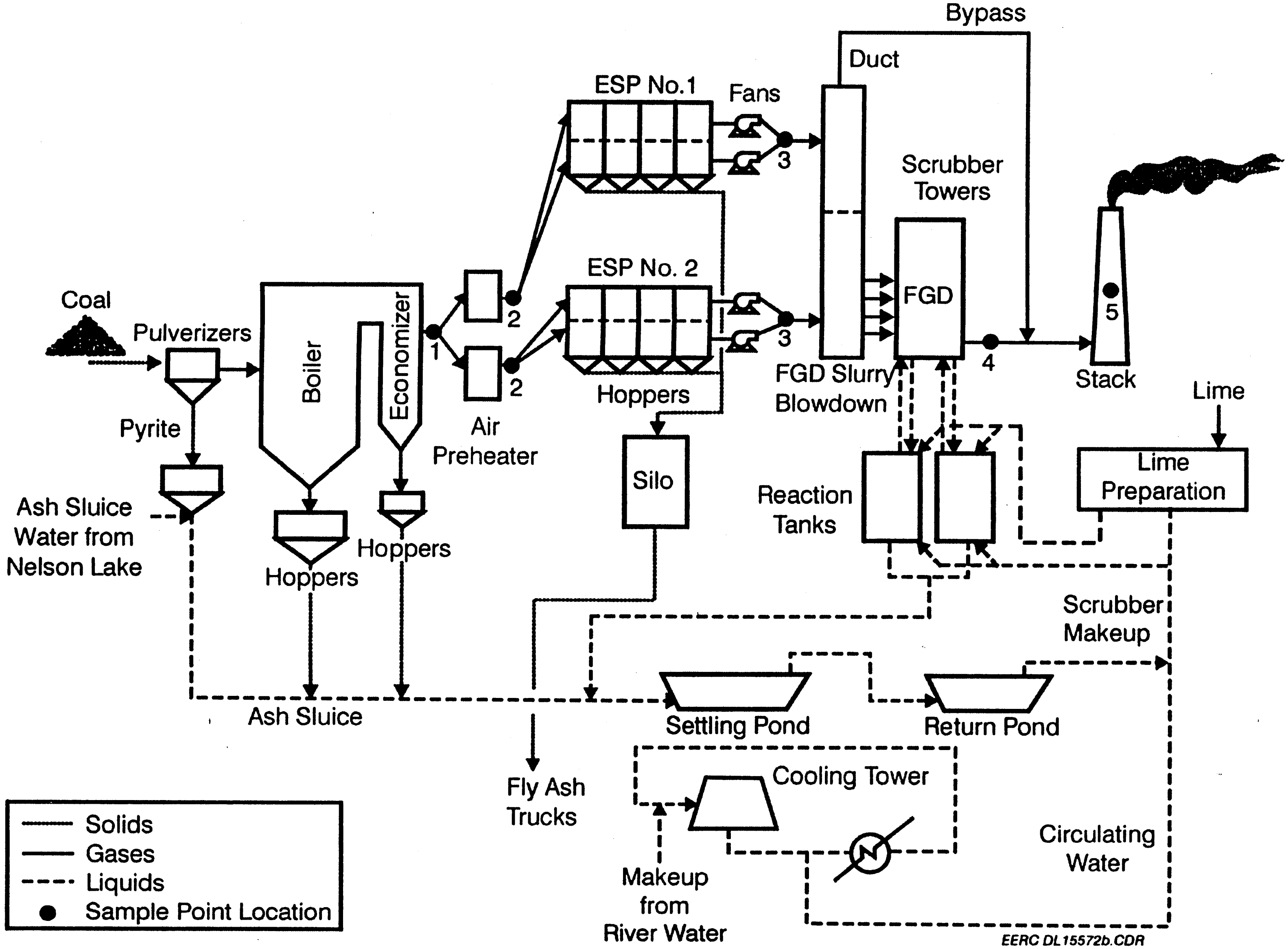

Figure 2-1. Schematic of Unit 2 at the Coal Creek Station (2)

Lignite is conveyed to the Coal Creek station from the nearby Falkirk mine by a conveyer system over 3 miles long. The lignite is crushed prior to being supplied to eight silos in each unit of the plant. The crushed lignite from the silos is then pulverized in eight 110-in.-diameter bowl mills manufactured by Combustion Engineering. The mills pulverize the coal to approximately 65% through a 200-mesh screen. Only seven of the eight mills are operating at any given time. The pulverized lignite is fed to the boilers pneumatically and injected into the furnace through the burners. It should be noted that the operation of the ball mills dries the coal to a great a extent. The Falkirk coal is about 35%–40% moisture as-mined; however, it is reduced to about 17% during pulverization. The coal feed rate is measured at the coal feeders, and the weighing system is calibrated quarterly. Based on a previous study at the Coal Creek Station (2) the estimated coal feed rate error is 0.14%.

Unit 2 is equipped with ESPs and FGD systems for removal of fly ash and sulfur dioxide (SO_2) from the boiler exhaust gases. Each of these air pollution control devices is described below.

2.1.1 Electrostatic Precipitator

Gas leaving Unit 2 travels through an economizer and then through two parallel air preheaters before entering two parallel halves of the ESP. Gas leaving the preheaters is divided into four ducts, two of which connect to each half of the ESP. The two shells of the ESP are constructed such that it can operate with one of the shells under reduced load. Each half of the ESP consists of six rows of four hoppers each, with one transformer/rectifier for each hopper. The design specifications for the ESP as a whole are shown in Table 2-1. The actual particulate collection efficiency during the testing is shown in Table 2-2. As this table shows, the measured particulate collection efficiency (>99.9%) during the testing period was well above the minimum specifications. This allowed the Coal Creek Station to easily meet the Federal Environmental Emission Standard of 0.1 lb of particulate matter per million Btu input. The fly ash collected in the ESP hoppers is stored in silos and sold for reuse.

2.1.2 *Flue Gas Desulfurization System*

To comply with environmental regulations for SO_2 emissions, Unit 2 has installed a wet-lime FGD system that was designed to remove 90% of the SO_2 from up to 60% of the flue gas flow. The system removes SO_2 from the flue gas by means of four countercurrent spray towers using a lime slurry. The remainder of the gas is recombined with the scrubbed gas to provide reheat. Flexibility in responding to changes in the fuel sulfur content is provided by a variable bypass system and by operating fewer than all four of the spray towers. The scrubber bypass flow can be adjusted by means of dampers in the flue gas flow line. The flow schematic of the FGD system is shown in Figure 2-1.

TABLE 2-1

ESP Design Specifications

ESP Parameter	**Specifications**
Total Gas Flow	2.3 million acfm
Nominal Operating Temperature	320°F
Nominal Operating Pressure	26.14 in. Hg
Specific Collection area (at nominal conditions)	599 ft^2/1000 acfm
Power Density	3.05 watt/ft^2
Gas Velocity	4.3 ft/sec
Residence Time	18 sec
Rated Particulate Collection Efficiency	99.5%

TABLE 2-2

ESP Particulate Collection Efficiency During the Week of Mercury Sampling

Day	**ESP Inlet Dust Loading, grains/scf**	**ESP Outlet Dust Loading, grains/scf**	**ESP Particulate Collection Efficiency, %**
2	3.3582	0.0012	99.96
2	4.0071	0.0016	99.96
3	5.0585	0.0009	99.98
3	5.8681	0.0014	99.98

Each spray tower has three levels of spray nozzles oriented countercurrent to the flue gas flow. To achieve the design SO_2 removal efficiency of 90%, the liquid-to-flue gas ratio is maintained at 60 gal/min per 1000 acfm. The flue gas leaving the scrubber is saturated with water vapor and is at a temperature of approximately 135°F. After this gas mixes with the remaining 40% unscrubbed flue gas, the temperature of the combined flue gas is about 200°–250°F at the stack inlet.

The lime slurry, which is made up as needed from a commercial lime and water from the cooling towers, local river, and return pond, is pumped to the spray towers from two slurry reactions tanks. The primary feedback loops for operation of the FGD system are pH, the SO_2 concentration in the stack, and the slurry level in the reaction tanks. Typically, the FGD is operated at a pH of about 7. This pH is maintained by the introduction of fresh slurry. Because the FGD system is designed as a zero discharge unit, the reacted slurry is recycled back to the FGD towers. A periodic blowdown is required to maintain the proper water level, suspended solids, and pH. The blowdown as well as the ash sluice is pumped to a settling pond. The water from the settling pond is then recycled to the FGD system.

2.2 Sampling Test Plan, Locations, and Collection Procedures

The locations of the flue gas-sampling points are represented by solid circles in Figure 2-1. As shown in the figure, the flow is split immediately after exiting from the boiler. The flue gas-sampling activities were completed along one of the gas steams. It was assumed that there was a good mixing of the flue gas and that the concentration of mercury in each of the gas streams was the same.

2.2.1 Flue Gas Sample Streams

The flue gas-sampling test plan is shown in Table 2-3. The primary flue gas sample streams of interest were the flue gas streams entering and exiting the ESP and FGD systems and the stack. The first four points determine the effectiveness of these air pollution control devices at removing targeted species of mercury released during coal combustion. Although these data are important to understanding the effects of air pollution control devices on mercury speciation, it is the mercury measurements at the stack that are of prime significance. Not only is it important to measure total mercury at the stack, but also the mercury speciation, because the rate of deposition of mercury in the environment is highly dependent on the type of mercury being emitted (3).

TABLE 2-3

Mercury Speciation Sampling Test Plan

Day	Air Preheater Inlet	ESP Inlet	ESP Outlet/ FGD Inlet*	FGD Outlet	Stack**
1		1	2	2	2
2	1	2	2	2	2
3	1	2	2	2	2
4		1			

*Three EPA Method 26A samples were also completed for chlorides.

**The Semtech Hg 2000 CEM was to be used to measure total mercury at the stack.

Mercury speciation measurements were also made at the inlet to the preheater and the stack. The purpose of sampling at the air preheater was to prove that at temperatures above about 800°F, the mercury is all in the elemental (Hg^0) form. In addition to mercury measurements, chlorides were also measured at the FGD inlet.

Although the original test plan included using an EPA Method 1 full-traverse sampling procedure, the availability of ports at some of the sampling locations made this impossible, as shown in Table 2-4. A one-dimensional traverse was made (one port, three locations) at the FGD outlet. A 12-point traverse grid was completed at the ESP inlet and the stack. A single-point sample was taken at the air preheater inlet, as well as for the chloride measurement. All sample locations were such that the sampling ports meet the EPA minimum requirements for upstream and downstream distance from the nearest flow disturbances. At the stack and at the ESP inlet, four ports were sampled located 90 degrees from each other. At the ESP outlet, only three ports were available for sampling.

2.2.2 Solid Sample Streams

In an effort to substantiate the flue gas mercury data, coal feed and ESP hopper ash samples were taken. These samples were analyzed for total mercury, and, along with the flue gas emissions data, were used to calculate the mercury mass balances. Table 2-5 shows the solid sample collection schedule. During pulverization of the coal, a cyclone separates the heavier material (referred to as pyrite) from the coal. This material is composed of iron compounds and

TABLE 2-4

Sampling Points Tested (traversing schedule)

Flue Gas Sample Location	Number of Points Sampled	Number of Ports Sampled
Air Preheater Inlet	1	1
ESP Inlet	3	4
ESP Outlet/FGD Inlet	3	3
FGD Outlet	3	1
Stack	3	4

TABLE 2-5

Solid Samples Collected at the Coal Creek Station

Sample No.	Date	Time	Type of Sample
1 – Coal Feed	8-4-98	1415	Falkirk ND lignite
2 – Coal Feed	8-5-98	730/1400	Falkirk ND lignite
3 – Coal Feed	8-6-98	750	Falkirk ND lignite
1 – Pyrite	8-4-98	1415	Extraneous material in coal
2 – Pyrite	8-5-98	730/1400	Extraneous material in coal
3 – Pyrite	8-6-98	750	Extraneous material in coal
1 – ESP Hopper 1	8-4-98	1740	Fly ash
2 – ESP Hopper 1	8-5-98	1210/1750	Fly ash
3 – ESP Hopper 1	8-6-98	1105/1800	Fly ash
1 – ESP Hopper 2	8-4-98	1745	Fly ash
2 – ESP Hopper 2	8-5-98	1610	Fly ash
3 – ESP Hopper 2	8-6-98	1145/1745	Fly ash
4 – ESP Hoppers 1–7	8-7-98	1805	Fly ash
1 – Lime Feed	8-4-98	725	Lime
2 – Lime Feed	8-5-98	854	Lime
3 – Lime Feed	8-6-98	742	Lime
1 – Grit	8-4-98	723	Extraneous material in lime
2 – Grit	8-5-98	850	Extraneous material in lime
5 – Grit	8-6-98	739	Extraneous material in lime

other relatively noncarbonaceous material. A total of six coal samples was collected. A composite sample was collected from each of the seven pulverizers daily. These six coal samples were analyzed for mercury. A typical coal analysis of this lignite is shown in Table 2-6.

ESP ash samples were taken at several locations. The design of the ESP made it very difficult to get ash samples from all of the ESP hoppers. During the first 2 days of sampling, only the first two hoppers were sampled. However, just prior to the sampling team's leaving, an ash sample was collected from seven of the ESP hoppers.

Other solid samples collected included the lime and grit material. Only one sample was analyzed from each, as the mercury the concentration in these samples was below the detection limits of the cold-vapor atomic absorption (CVAA) instrument. Therefore the concentration of mercury in these samples was considered insignificant in determining the mercury mass balances.

TABLE 2-6

Analysis of the Falkirk, North Dakota, Lignite on a Dry Basis

Proximate Analysis, wt%	
Moisture Content	16.80
Volatile Matter	46.12
Fixed Carbon	36.90
Ash	16.98
Ultimate Analysis, wt%	
Hydrogen	4.20
Carbon	58.39
Nitrogen	0.85
Sulfur	0.96
Oxygen, by difference	18.63
Ash	16.98
Heating Value, Btu/lb	10,135
Coal Ash Analysis, % conc. as oxides	
SiO_2	31.8
Al_2O_3	11.7
Fe_2O_3	6.4
TiO_2	0.5
P_2O_5	0.3
CaO	17.0
MgO	6.5
Na_2O	2.9
K_2O	1.3
SO_3	16.0

2.2.3 Liquid Sample Stream

The liquid samples collected during the test program are shown in Table 2–7. The lime slurry samples were collected from the reaction tanks and the FGD slurry samples were collected from the slurry recycle stream. Assuming the system has reached a steady state, the concentration of mercury in the recycle will be the same as in the blowdown.

2.3 Process Operation During Testing

Tables 2-8 and 2-9 summarize the process operating conditions and gas emissions during the mercury speciation test program. As these tables show, operation of Unit 2 during this test program was representative of normal daily operation at or near full load and there was little variation in the 5 days of the test program. SO_2 and particulate emissions were in compliance, with no ESP operating problems identified.

TABLE 2-7

Liquid Samples Collected at the Coal Creek Station

Sample No.	Date	Time	Type of Sample
1 – Lime Slurry Feed	8-4-98	732/1359	Lime + ash pond water
2 – Lime Slurry Feed	8-5-98	856/1355	Lime + ash pond water
3 – Lime Slurry Feed	8-6-98	740/1333	Lime + ash pond water
1 – Makeup Water	8-4-98	705/1404	Ash pond water
2 – Makeup Water	8-5-98	900/1359	Ash pond water
3 – Makeup Water	8-6-98	745/1336	Ash pond water
1 – FGD Slurry	8-4-98	707/1406	Reacted FGD slurry
2 – FGD Slurry	8-5-98	904/1400	Reacted FGD slurry
3 – FGD Slurry	8-6-98	749/1340	Reacted FGD slurry
1 – River Water	8-4-98	809	River water
2 – River Water	8-5-98	935	River water
3 – River Water	8-6-98	842	River water
3 – Ash Pond Water	8-6-98	1415	Ash pond water

TABLE 2-8

Average Coal Creek Unit 2 Operating Conditions Summary

Date	Gross Load, MW	Total Coal Flow, klb/hr	Total Gas Flow at the Stack, kscfm	Main Steam Flow, klb/hr	Steam Throttle Temp., °F	Reheat Outlet Temp., °F	Scrubber Bypass Temp., °F	Scrubber Module Temp., °F	Stack Temp., °F
8-4-98	588.9	887.8	1707.7	4072.9	995.9	1006.8	312.8	139.5	242.3
8-5-98	588.8	887.8	1657.7	4072.8	995.9	1006.9	319.5	140.1	249.5
8-6-98	587.9	937.0	1656.0	4074.5	995.6	1004.7	316.8	139.7	239.2
8-7-98	589.5	939.6	1696.6	4075.0	995.7	1006.0	309.7	139.5	231.4

TABLE 2-9

Average Coal Creek Unit 2 Flue Gas Emissions

Date	Boiler O_2, %	Stack CO_2, %	Stack NO_x, ppm	Scrubber Inlet SO_2, ppm	Stack SO_2 Emissions, ppm	SO_2* Emission Rate, lb/MMBtu	NO_x Emission Rate, lb/MMBtu	Opacity, %
8-4-98	3.3	12.1	124.8	581.6	422.0	1.07	0.24	4.5
8-5-98	3.3	12.1	121.8	581.6	429.2	1.07	0.24	4.5
8-6-98	3.3	12.1	119.3	581.6	425.4	1.07	0.23	4.5
8-7-98	3.3	12.0	138.6	555.4	425.9	1.07	0.27	4.8

* The plant is required to meet an SO_2 emission rate of 1.2 lb/MMBtu.

The target excess O_2 at the boiler exit was to be 3.5% ± 0.5%. As Table 2-8 shows, the unit easily fell within this range. The average excess O_2 for the entire 4-day sampling period was 3.3% ± 0.06%. The average O_2 levels and moisture content at each of the flue gas sampling points are shown in Table 2-10. On the basis of the O_2, data, there is a substantial air leak across the air preheater.

3.0 FLUE GAS SAMPLING AND ANALYTICAL METHODS

This section describes the methods and analytical procedures that were that were used for this test program to determine the mercury speciation and chlorides in the flue gas, as well as the total mercury in the solid and liquid streams of the plant. The details of all the EPA sampling

TABLE 2-10

Average Excess Oxygen and Moisture Content at Mercury Speciation Sampling Points

Sample Location	Excess O_2 (on a dry basis),%	Moisture Content, %
Boiler	3.3	13.8
Air Preheater Inlet	3.5	15.9
ESP Inlet	6.0	15.4
ESP Outlet/FGD Inlet	5.8	14.6
FGD Outlet	5.8	20.9
Stack	5.7	17.5

procedures discussed in the section (EPA Methods 1–4, 5, 17, 29, and 26A) can be found on the EPA Emission Measurement Center Web site at the address http://www.epa.gov/ttn/emc.

One issue that has been extensively discussed with respect to mercury speciation methods is the temperature at which the particulate filter should be maintained. On the basis of current procedures, the requirement is that the filter and sample probe be maintained at the flue gas temperature. For all of the flue gas mercury sampling that was completed for this project, an EPA Method 17 in-stack borosilicate glass filter was used. This ensured that the filter and probe were maintained at the flue gas temperature. The only exception to this was at the FGD outlet. At this location, the high moisture content of the gas stream required that the filter be out of stack to ensure that no moisture condensation occurred at the filter. Therefore, a long heated probe was used and the filter was maintained at 300°F using a heated muff.

All components of the sample train were composed of either glass or Teflon. The length of the probes at each of the flue gas sample points is shown in Table 3-1.

TABLE 3-1

Probe Length at Each Sample Point

Sample Point	Probe Length, ft
Air Preheater	6
ESP Inlet	11
ESP Outlet	9
FGD Outlet	9
Stack*	13

* Stack diameter at the sampling point was 22 ft.

3.1 Ontario Hydro Mercury Speciation Method

The Ontario Hydro method was developed by Keith Curtis and other researchers at Ontario Hydro Technologies in late 1994. Since testing with EPA Method 29 appeared to show that some of the Hg^0 was captured in the nitric acid–hydrogen peroxide (HNO_3–H_2O_2) impingers, an attempt was made to more selectively capture the oxidized mercury (Hg^{2+}) by substituting three aqueous 1N potassium chloride (KCl) impinger solutions for one of the HNO_3–H_2O_2 solutions. A schematic of the impinger train is shown in Figure 3-1. The Ontario Hydro method has been extensively tested at the EERC and has been shown to provide the best mercury speciation data for coal-fired boilers (4, 5). The method is currently being evaluated by the American Society for Testing and Materials (ASTM) Subcommittee D22.03.01. A description of the Ontario Hydro Method in the ASTM format is available on the EPA Web site at http://www.epa.gov/ttn/emc under Preliminary Methods.

All glassware for the sample trains was precleaned with using a 4-hr soak in a 10% HNO_3 solution, with no impinger glassware used more than once in the field test. Samples collected using the Ontario Hydro method were recovered into the following fractions:

- Probe ash and particulate filter and ash – Container No. 1
- Probe rinse with 0.1 N HNO_3 solution – Container No. 2A

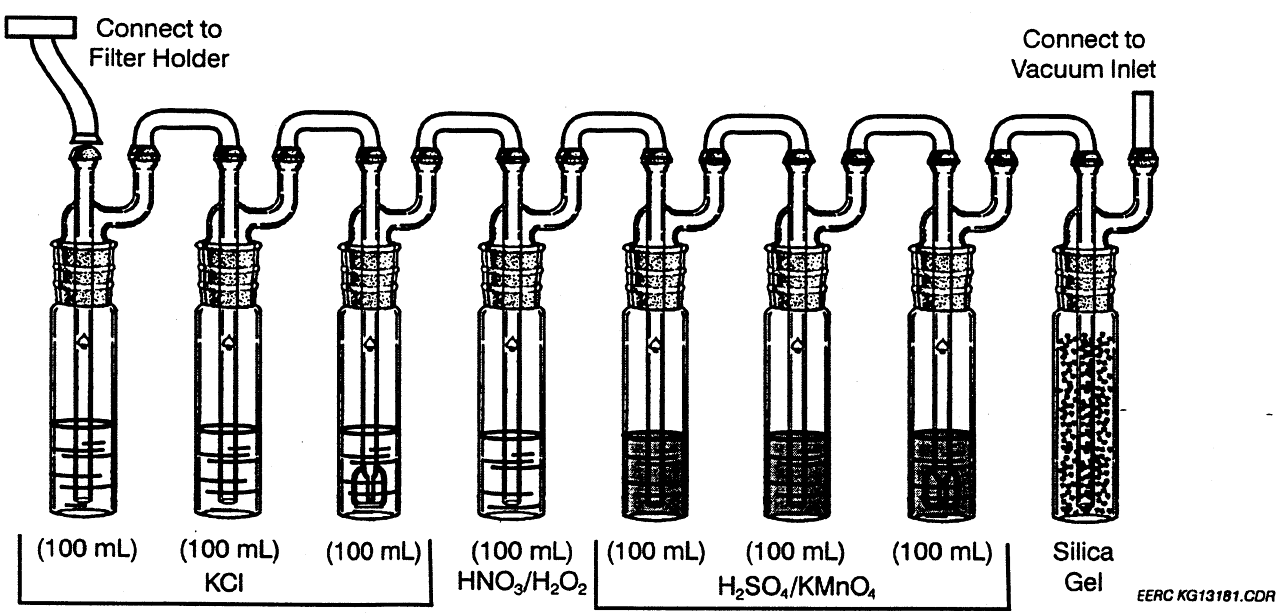

Figure 3-1. A schematic of the Ontario Hydro impinger train.

- Back half of the filter holder and connecting U-tubes 0.1 N HNO_3 rinses plus the three KCl impinger solution and their 0.1 N HNO_3 rinses – Container No. 2B
- The HNO_3–H_2O_2 solution and its 0.1 N HNO_3 rinse and the rinse of the U-tube between the last KCl impinger and H_2O_2 – Container No. 3
- H_2SO_4–$KMnO_4$ impinger and rinses (0.1 N HNO_3 rinses and 8 N HCl rinses) and the rinse of the U-tubes rinses – Container No. 4

The solutions were analyzed on-site using a Leeman CVAA instrument. The particulate fraction, which was taken back to the EERC, was analyzed first using a HCl/HF microwave digestion procedure followed by CVAA analysis for mercury. A schematic of the teardown of the sample train and the various fractions is shown in Figure 3-2

For the each of the three liquid solutions of the Ontario Hydro method, prior to analyses, a different preparation procedure must be used. The preparation steps for each solution are described below:

KCl solution. The KCl sample fractions are immediately preserved with acidified $KMnO_4$ after sampling. This solution is then digested using a potassium persulfate digest procedure.

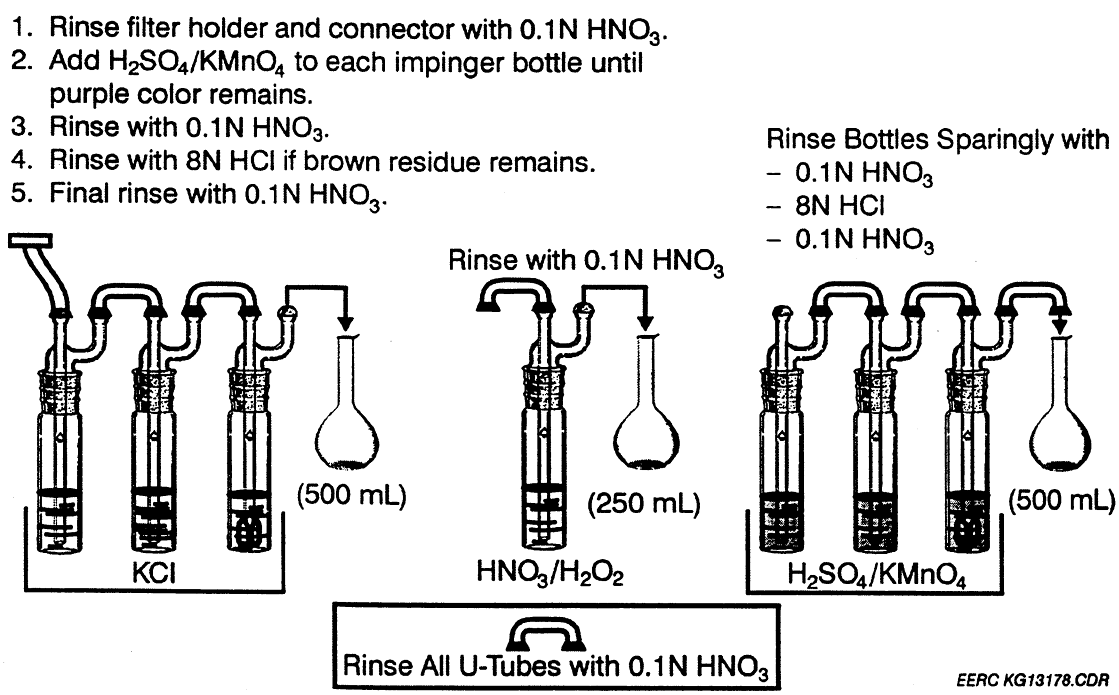

Figure 3-2. A schematic of the impinger train teardown procedures.

HNO_3–H_2O_2 solution. The solution is first preserved with 10% $^v/_v$ HCl, then combined with H_2SO_4–$KMnO_4$ solution until a purple color persists. At this point, hydroxylamine sulfate is added until the solution becomes clear.

H_2SO_4–$KMnO_4$ solution. Hydroxylamine sulfate is added to the $KMnO_4$–H_2SO_4 sample until the solution turns clear.

For the Ontario Hydro method, the KCl fraction results are reported as Hg^{2+}, and the sum of the mercury measured in the HNO_3–H_2O_2 solution and H_2SO_4–$KMnO_4$ solution is reported as Hg^0. The mercury measured on the filter ash is defined as particulate-bound mercury. The exact form of the mercury on the particulate matter is still unknown. For these tests, since EPA Method 17 was followed (filter holder is placed in the duct), the mercury found in the probe rinse was insignificant.

3.2 EPA Method 26A

To measure concentration of chlorides in the flue gas, EPA Method 26A was used. A schematic of the train is shown in Figure 3-3. This method was designed to measure both the HCl and Cl_2 concentrations in the flue gas. During the sampling, the separation of the halides (HCl) from the halogens (Cl_2) is accomplished physically within the impinger matrices. Cl_2 exhibits a low solubility in acid solutions (0.1 N H_2SO_4), but is collected effectively in basic solutions (0.1 N NaOH). The HCl, on the other hand, is captured effectively by the 0.1 N H_2SO_4 solution. The impinger train is operated similarly to other sampling procedures such as EPA Method 5 or EPA Method 29.

Once the chlorides were collected in the solutions, they were analyzed using ion chromatography techniques. Prior to analysis, the 0.1 N H_2SO_4 solution was passed through an ion-exchange resin to convert any chloride salts back to the acid and also to remove any calcium or iron that might have been captured in the solution, as these may cause scaling in the chromatography column. Preparation of the 0.1 N NaOH solution was done by adding sodium thiosulfate to the solution to reduce any hypohaleous acid that might form.

3.3 Semtech Hg 2000 Analyzer

A Semtech Hg 2000 mercury CEM manufactured by Semtech Metallurgy AB, Lund, Sweden, was used at the stack location. The instrument measures Hg^0 on a real-time basis using a

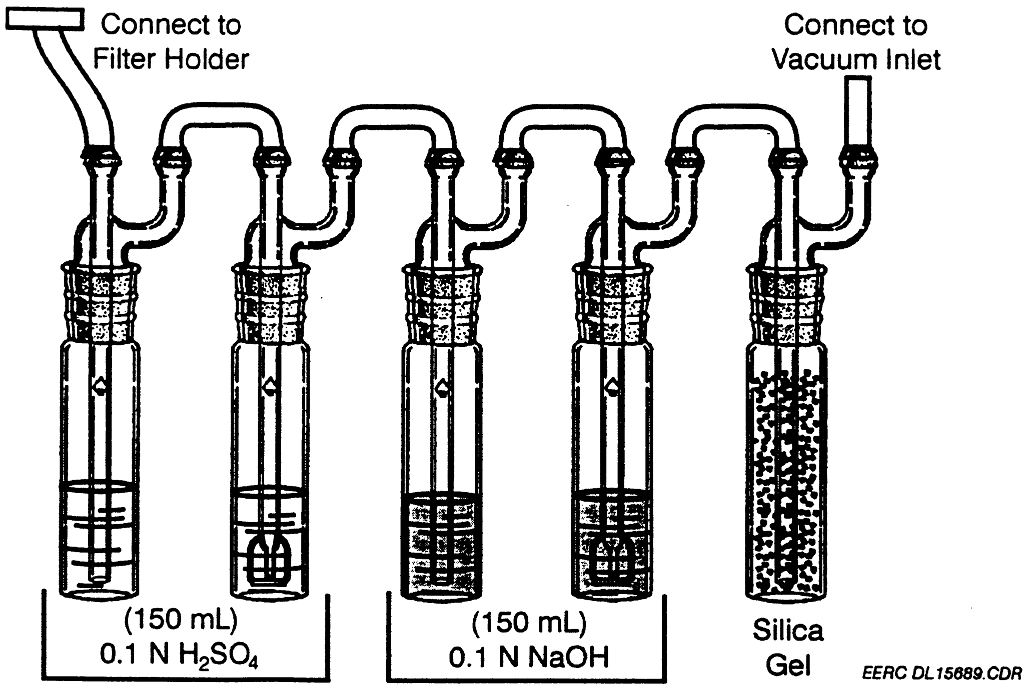

Figure 3-3. A schematic of the EPA Method 26A impinger train that was used for chloride measurement.

Zeeman-shifted ultraviolet sensor. The Zeeman shift detection technology eliminates interference from SO_2 absorption. Because the instrument is designed to measure only Hg^0, to get total mercury the other forms of mercury (Hg^{2+}) must be converted to Hg^0. This is done by passing the flue gas through a stannous chloride solution prior to its entering the CEM. The operating range of the instrument is 0.3 $\mu g/Nm^3$ to 20 mg/Nm^3. The Semtech Hg 2000 has been certified by TUEV Rheinland for determining compliance with the German legal limit of 50 $\mu g/Nm^3$ for total mercury from waste incinerators.

3.4 Oxygen Concentration, Flue Gas Velocity, and Moisture

To determine the O_2 levels at each sample location, a Teledyne portable O_2 analyzer using a paramagentic cell was used. This portable O_2 analyzer's linearity was verified prior to our using EPA Protocol 1 certified gas standards. In addition, the plant has O_2 CEMs that give the O_2 concentration at the outlet of the boiler. Therefore, any leaks into the ducts at each of the sample points could be determined. For the purposes of this report, the mercury concentrations are reported on a constant-O_2 basis (3% O_2).

Flue gas velocity, moisture, and flow rate determinations were performed according to EPA Methods 2 and 4 in conjunction with the Ontario Hydro method.

3.5 Quality Assurance/Quality Control

An overall quality assurance/quality control (QA/QC) program in place at the EERC is designed to maintain overall data integrity. However, additional procedures were instituted specifically for this project.

3.5.1 Instrument Setup and Calibration

The instrument used in the field for mercury determination was a Leeman Labs PS200 CVAA. To measure mercury, the instrument was set up for absorption at 253.7 nm with a carrier gas of nitrogen and 10% $^{w}/_{v}$ stannous chloride in 10% $^{v}/_{v}$ HCl as the reductant. Each day the drying tube and acetate trap were replaced and the tubing checked. The rinse container was cleaned and filled with fresh solution of 10% $^{v}/_{v}$ HCl. After the pump and lamp were turned on and warmed up for 45 minutes, the aperture was set to the manufacturer specifications. A four-point calibration curve was then completed using matrix-matched standards. The detector response for a given standard was logged and compared to specifications to ensure the instrument had been properly set up. A quality control standard of a known analyte concentration was analyzed immediately after the instrument was standardized in order to verify the calibration. This quality control standard was prepared from a different stock than the calibration standards. It was required the values obtained read within 5% of the true value before the instrument was used. After the initial QC standardizations were completed, standards were run every five samples to check the slope of the calibration curve. All samples were run in duplicate, and one in every ten samples was spiked to verify analyte recovery. A QC chart is maintained at the EERC to monitor the long-term precision of the instrument.

Prior to the testing, all gas-sampling equipment was calibrated according to the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III. Stationary Source Specific Methods*. The uncertainty of the individual measurements was determined using the performance test codes in ANSI/ASME PTC 19.1-1985, Part 1, Measurement Uncertainty, as a guideline.

3.5.2 Presampling Preparation

All data sheets, volumetric flasks, and petri dishes used for sample recovery were marked with preprinted labels. The liquid samples were recovered into premarked volumetric flasks and logged, then analyzed on-site. The filter samples were placed in premarked petri dishes and taken back to the EERC, where they were analyzed using mixed acid digestion techniques. The labels contained identifying data, including date, time, run number, sample port location, and the name of the sampler.

3.5.3 Glassware and Plasticware Cleaning and Storage

All glass volumetric flasks and transfer pipets used in the preparation of analytical reagents and calibration standards were designated Class A to meet federal specifications. Prior to being used for the sampling, all glassware was washed with hot, soapy water, then rinsed with deionized water three times, soaked in 10% $^{v}/_{v}$ nitric acid for a minimum of 4 hours, rinsed an additional three times with deionized water, and dried. The glassware was then stored in closed containers until it was used at the plant.

3.5.4 Analytical Reagents

All acids that were used for the analysis of mercury were trace metal grade. Other chemicals that were used in the preparation of analytical reagents were analytical reagent grade. The calibration standards used for instrument calibration and the QC standards used for calibration verification were purchased commercially and certified to be accurate within ±0.5% and were traceable to National Institute of Standards and Technology (NIST) Standard Reference Materials.

3.5.5 Blanks

As part of the QA/QC procedures, a field blank was associated with sampling. A field blank is defined as a complete impinger train, including all glassware and solutions, that is taken out to the field during sampling and exposed to ambient conditions. These sample trains are then taken apart and the solutions recovered and analyzed in the same manner as those sample trains used for sampling activities. If the field blank shows contamination above instrument background, steps must be taken to eliminate or reduce the contamination to below background levels. However, in all cases the fields blanks taken during the sampling activities at the Coal Creek Station were shown to be insignificant, as shown in Table 3-2.

TABLE 3-2

Results for Mercury Speciation Field Blanks

Day	KCl Solution, μg/L	H_2O_2 Solution, μg/L	$KMnO_4$ Solution, μg/L
1	<0.1	<0.1	<0.1
2	<0.1	<0.1	<0.1
3	<0.1	<0.1	<0.1

All acids, chemical reagents, and deionized water used for mercury determination were analyzed for background levels of mercury. Each time a new batch of reagents was prepared, an aliquot was immediately taken and analyzed for mercury. Again, no mercury contamination was found.

3.5.6 Spiked Samples

In order to ensure that adequate levels of accuracy were maintained, spiked samples were also submitted for analysis. These samples were made up independently of the chemist doing the analyses. The spikes were required to be within 15% of the true value. The spiking solutions were from a stock separate from the calibration standard stock. The analytical results for the spiked samples are shown in Table 3-3. As can be seen, with only a few exceptions, the analyses of these spikes are within the tolerance specified.

4.0 MERCURY RESULTS

Coal mercury. The mercury analysis of the Falkirk coal is shown in Table 4-1. The mercury averaged 98 ppb for the six coal samples, with a variation of 7.4 ppb. This is excellent reproducibility, as the mercury in coal tends to be quite variable and getting representative samples can be very difficult.

The mercury concentration was also measured in the pyrite catch. Although the concentration of mercury in this material was more than an order of magnitude higher than in the coal, 2.4 μg/g compared to about 0.1 μg/g for the coal, the amount of material collected as pyrite is very low. Therefore, the total amount of mercury removed in the pyrite catch is insignificant.

TABLE 3-3

Results of Mercury Speciation Field Spikes

	KCl Solution			H_2O_2 Solution			$KMnO_4$ Solution		
Date	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %	Measured Value, ppb	Spike, ppb	Spike Recovery, %
8-4-98	10.49	10	104.9	10.91	10	109.1	8.94	10	89.4
8-4-98	5.19	5	103.9	9.8	10	98.0	4.56	5	91.2
8-4-98	10.65	10	106.5	5.62	5	112.4	4.14	5	82.8
8-4-98	5.63	5	112.6						
8-4-98	11.22	10	112.1						
8-5-98	9.77	10	97.7	10.57	10	105.7	9.56	10	95.6
8-5-98	4.23	5	84.6	10.78	10	107.8	10.22	10	102.2
8-5-98	7.31	10	73.1	5.66	5	113.2	5.10	5	102.0
8-5-98	9.37	10	93.7	9.26	10	92.6	4.77	5	95.4
8-5-98	4.80	5	96.0						
8-5-98	9.49	10	94.9						
8-6-98	9.42	10	94.2	8.78	8	109.7	9.25	10	92.5
8-6-98	4.20	5	84.0	10.72	10	107.2	4.65	5	93.0
8-6-98	6.79	10	67.9	5.46	5	109.2	4.41	5	88.2
8-6-98	4.93	5	98.6	5.55	5	111.0	4.47	5	89.4
8-6-98	9.16	10	91.6				3.80	5	76.0
8-6-98	8.42	10	84.2						
8-6-98	5.70	5	114.0						
8-6-98	10.79	10	107.9						
	Average		95.9	Average		106.9	Average		91.5
	Std. Dev.		12.9	Std. Dev.		6.3	Std. Dev.		7.4

ESP ash and sample filter mercury. The mercury collected on the filter of the sample trains at the ESP inlet was very low. In all cases, it was below the lower limit of quantification of the instrument, which is 0.01 µg Hg/g ash. These results are the same as the mercury in the ESP hopper ash, which was also below 0.01 µg/g. These data show that there was essentially no mercury removed across the ESP. This was in agreement with the test on Unit 1 of the Coal Creek Station that was done by Battelle for DOE in 1994 (2).

TABLE 4-1

Mercury in the Falkirk Coal

Day	Coal Hg Concentration, ppb
1	98
1	88
2	93
2	98
3	100
3	110
Average	98 ± 7.4

It should be noted that the mercury on the filters at all other sampling points was not analyzed because the particulate removal efficiency of the ESP was very high, > 99.9%, and the mercury analyses of filters at the ESP inlet showed no mercury associated with the ash. Therefore, the amount of measured mercury would have been well below the detection limit of the instrument. In addition, the uncertainty of the data would be very high.

FGD slurry mercury. An FGD slurry can either be a reacted or unreacted slurry. The unreacted slurry is made up of the fresh lime and water that comes from the ash pond and river. The reacted slurry is the lime and water after being in contact with the SO_2-containing flue gas. At the Coal Creek Station, the reacted slurry is recycled to the FGD system, with periodic blowdown to maintain the proper water level and solution pH. The mercury concentration in slurry was determined by the concentration of mercury in solids and the mercury concentration in the water. The mercury concentration of the blowdown was assumed to be the same as the mercury concentration in the recycled reacted slurry. The concentration of mercury in each fraction of the FGD slurries is shown in Table 4-2. As the table shows, there was essentially no mercury in the fresh lime slurry.

The mercury concentration was also determined in the ash pond makeup water, the ash sluice water, and river water because these water sources make up the unreacted slurries. The mercury concentration in the water from all three sources was <0.1 μg/L.

4.1 Mercury Speciation Results

This section presents the flue gas mercury speciation results across the ESP and FGD systems. The mercury speciation results are shown in Table 4-3. All data are based on 68°F, dry conditions and are adjusted to 3% oxygen. Figures 4-1 and 4-2 show the mercury removal across the ESP and FGD systems. The original data sheets for the flue gas mercury can be found in Appendix A. Examples of the calculations used in this report are shown in Appendix B. All the mercury data were averaged, and a standard deviation was calculated. As can be seen from the table, the data variability was low (usually less than 10%). Therefore, process conditions of the plant were relatively constant and had little effect on mercury measurements.

Comparing the ESP inlet and outlet mercury concentrations (shown in Table 4-3 and Figure 4-1) it appears that no mercury is removed across the ESP. However, it is clear that Hg^0 was converted to Hg^{2+} across the ESP. There are three times as much Hg^{2+} at the ESP outlet compared to the inlet (1.00 μg/Nm^3 compared to 3.00 μg/Nm^3). Evidence has been presented in the literature showing some conversion of mercury species can occur across an ESP (6).

TABLE 4-2

Mercury Concentrations in the FGD Slurries

Unreacted Slurry		Reacted Slurry	
Solid, μg/g	**Liquid, μg/L**	**Solid, μg/g**	**Liquid, μg/L**
<0.01	<0.01	0.656	0.95
<0.01	<0.01	0.646	0.53

Table 4-3 clearly shows that the FGD system effectively removed the Hg^{2+}, but little if any Hg^0. This is in agreement with all the mercury data that have been collected in the last several years across wet FGD systems. The speciated mercury emissions at the stack show that a substantial portion of the flue gas bypasses the scrubber system. The Hg^{2+} concentration in the stack is about 50% of the concentration at the FGD inlet.

TABLE 4-3

Mercury Speciation Results across the ESP and FGD Systems

	ESP Inlet				ESP Outlet		
	Total Hg, µg/Nm³	Particulate-Bound Hg, µg/Nm³	Hg^0, µg/Nm³	Hg^{2+}, µg/Nm³	Total Hg, µg/Nm³	Hg^0, µg/Nm³	Hg^{2+}, µg/Nm³
	11.90	<0.1	9.88	2.02	10.91	8.54	2.37
	11.84	<0.1	10.96	0.88	12.07	8.39	3.67
	11.34	<0.1	10.67	0.67	11.75	8.75	3.00
	14.50	<0.1	13.83	0.66	11.10	8.12	2.98
	11.69	<0.1	11.05	0.64	10.85	7.54	3.30
	11.68	<0.1	10.57	1.11	10.97	8.28	2.69
Average	12.16	<0.1	11.16	1.00	11.27	8.27	3.00
Std. Dev.	1.16		1.37	0.53	0.51	0.42	0.46

	FGD Inlet			FGD Outlet			Stack		
	Total Hg, µg/Nm³	Hg0, µg/Nm³	Hg^{2+}, µg/Nm³	Total Hg, µg/Nm³	Hg^0, µg/Nm³	Hg^{2+}, µg/Nm³	Total Hg, µg/Nm³	Hg^0, µg/Nm³	Hg^{2+}, µg/Nm³
	10.91	8.54	2.37	8.96	8.95	0.01	10.27	8.54	1.73
	12.07	8.39	3.67	9.36	9.24	0.12	10.70	8.43	2.26
	11.75	8.75	3.00	8.13	7.91	0.22	11.74	9.86	1.88
	11.10	8.12	2.98	8.58	8.28	0.30	11.70	9.61	2.09
	10.85	7.54	3.30	8.29	8.13	0.16	8.83	6.97	1.86
	10.97	8.28	2.69	9.75	9.64	0.10	12.06	10.24	1.82
Average	11.27	8.27	3.00	8.84	8.69	0.15	10.88	8.94	1.94
Std. Dev	0.51	0.42	0.46	0.63	0.69	0.10	1.22	1.21	0.20

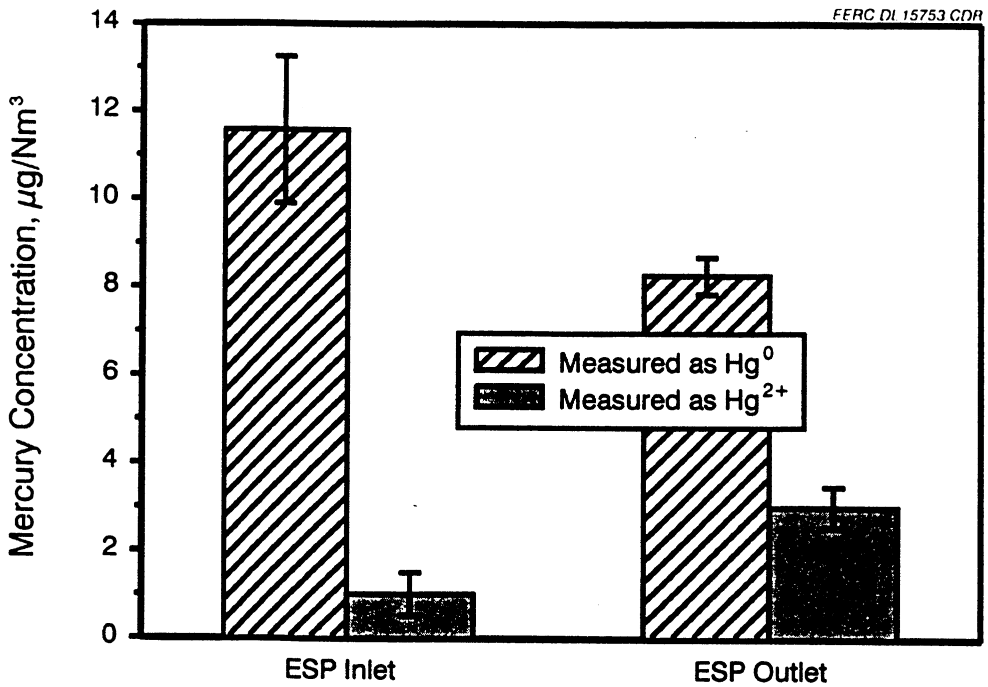

Figure 4-1. The change in vapor-phase speciated mercury across the ESP.

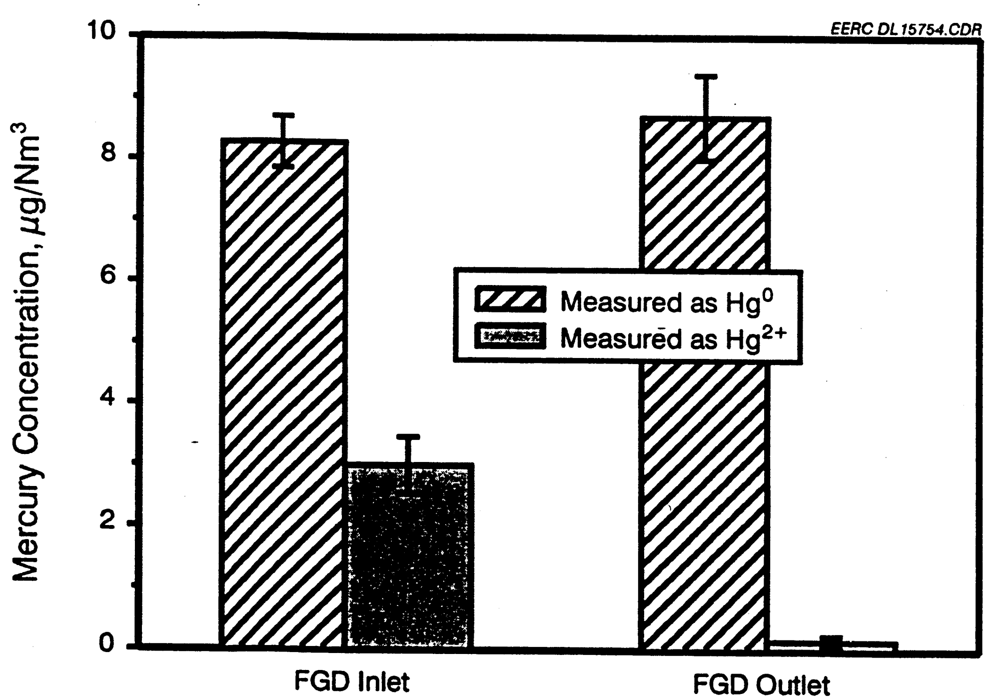

Figure 4-2. The change in vapor-phase speciated mercury across the FGD system.

Two Ontario Hydro method samples were completed at the inlet to the air preheater. The temperature at this location was about 800 °F. The purpose of these samples was to determine if the Hg^{2+} was present in the flue gas these temperatures. Although, the mercury in the flue gas at the inlet to air preheater was about 95% Hg^0 compared to 92% Hg^0 at the ESP inlet where the temperature was 320°F, it was expected that an even higher percentage would be Hg^0. This would suggest that Hg^{2+} mercury compounds begin to form at higher temperatures than were thought. The data are shown Appendix A.

Because it is thought the level of chlorides in the flue gas stream may influence mercury speciation, four EPA Method 26A sample trains were completed at the inlet to the FGD system. This sample method was designed to measure both the HCl concentration in the gas stream and the Cl_2. In practice, the method does not work very well as a chloride speciation measurement method, but does provide a good measurement of the total chloride concentration in the flue gas. The EPA Method 26A results are shown in Table 4-4. As shown, the chloride concentration is very low. This is typical of all western fuels (both lignites and subbituminous). For these fuels, the chloride concentration is usually less then 5 ppm. Although the chloride concentration in the flue gas is low, it is still several orders of magnitude higher than the mercury concentration. However, this does bring up the question of whether the actual Hg^{2+} compound being measured is $HgCl_2$ as thought.

4.2 Semtech Hg 2000 CEM Results

The Semtech CEM was used only at the stack. Although the instrument was developed to measure only Hg^0, using a conversion system designed at the EERC the instrument was able to measure total mercury. For this project, it was originally intended that the Semtech CEM would provide mercury speciation data. This was to be accomplished by bypassing the conversion system periodically to measure Hg^0 and by difference determining the concentration of Hg^{2+} in the flue gas. However, because of the high moisture content of the flue gas, the instrument would not operate properly without first passing through the conversion system where a chiller removed the moisture. A comparison between the Semtech CEM data and the Ontario Hydro method data is shown graphically in Figures 4-3 through 4-5. As can be seen from the three graphs, the CEM results compare very well with the results obtained using the Ontario Hydro method.

TABLE 4-4

Chloride Concentrations in the Flue Gas at the FGD Inlet

Day	HCl Concentration, ppm	Cl_2 Concentration, ppm
1	0.66	0.33
2	0.94	0.47
3	0.45	0.22

4.3 Emission Factors

The emission factors at the stack of Unit 2 are shown in Table 4-5. The emission factors averaged 8.57 lb of Hg/10^{12} Btu, with a standard deviation of 1.01 lb of Hg/10^{12} Btu. About 80 % of the total mercury emissions at the stack was Hg^0, and 20% was Hg^{2+}. The particulate-bound mercury was insignificant (less than the detection limits). On the basis of results reported in *A Comprehensive Assessment of Toxic Emissions from Coal-Fired Power Plants* (7), these

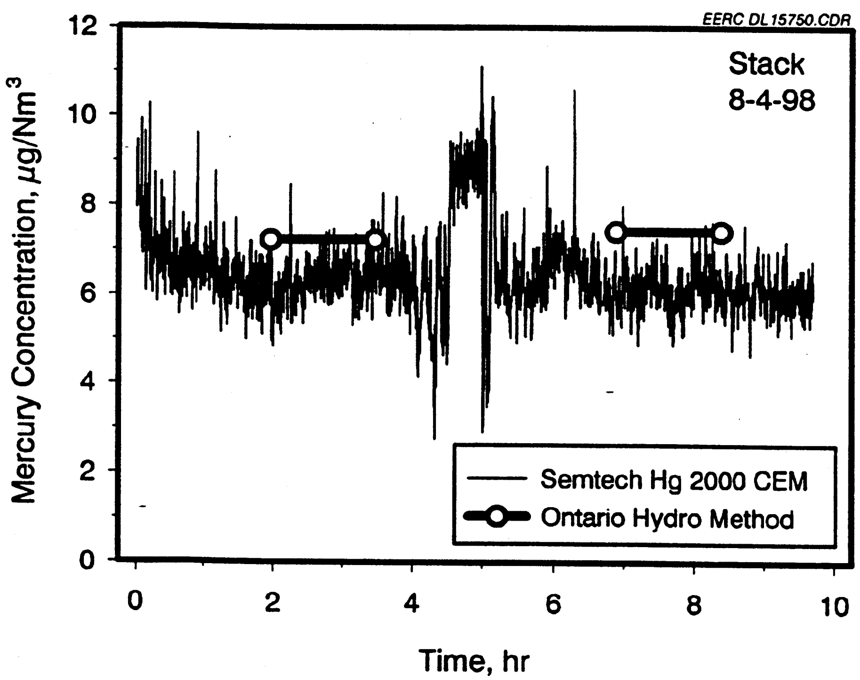

Figure 4-3. Direct comparison between Semtech CEM and the Ontario Hydro Method for Day 1 (data are shown as measured at the stack).

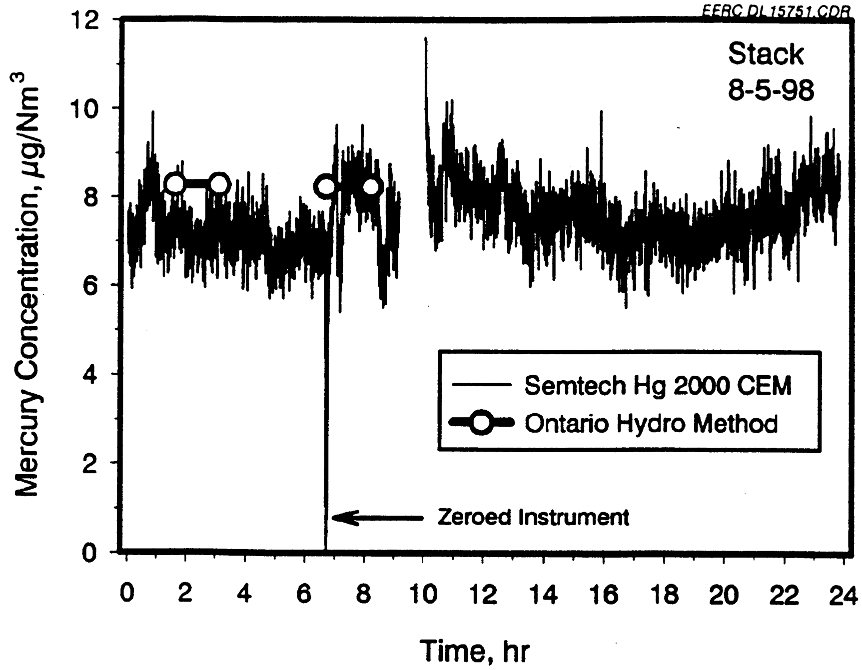

Figure 4-4. Direct comparison between Semtech CEM and the Ontario Hydro method for Day 2 (data are shown as measured at the stack).

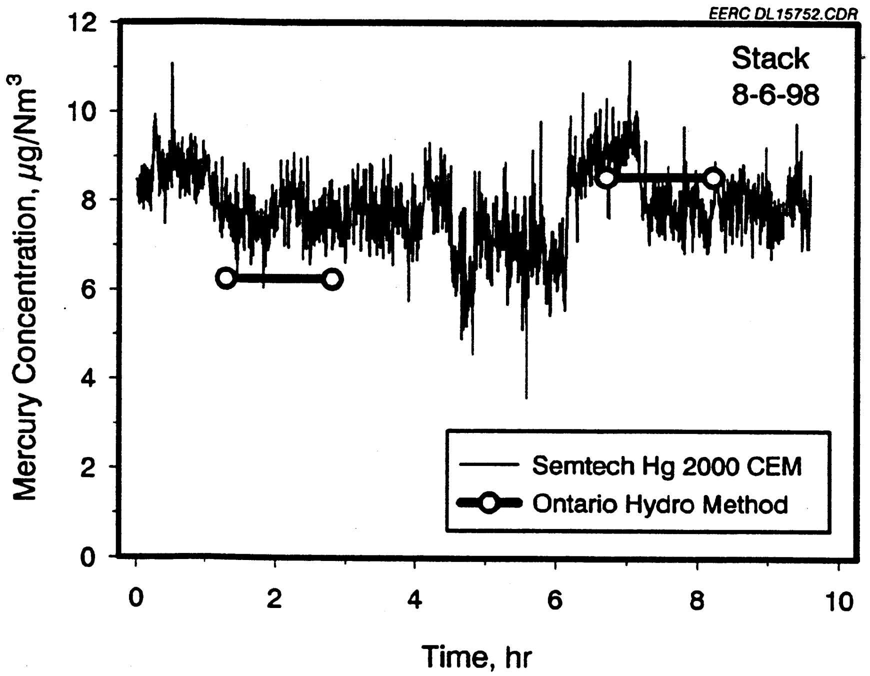

Figure 4-5. Direct comparison between Semtech CEM and the Ontario Hydro method for Day 3 (data are shown as measured at the stack).

TABLE 4-5

Mercury Emission Factors at Coal Creek's Unit 2 Stack

				Emission Factors		
Sample*	Coal Feed Rate, klb/hr	Coal Heating Value, Btu/lb	Stack Gas Flow Rate, kscfm	Hg^{2+}, lb/10^{12} Btu	Hg^0, lb/10^{12} Btu	Total Hg, lb/10^{12} Btu
1	887.8	6175	1707.7	1.40	6.98	8.38
2	887.8	6175	1707.7	1.82	6.82	8.64
3	887.8	6175	1657.7	1.49	7.83	9.32
4	887.8	6175	1657.7	1.66	7.65	9.31
5	937.0	6180	1656.0	1.39	5.27	6.66
6	937.0	6180	1656.0	1.37	7.76	9.13

* Samples 1 and 2 were taken 8-4-98, Samples 3 and 4 on 8-5-98 and Samples 5 and 6 on 8-6-98.

emission factors are fairly typical for coal-fired boilers. The results from this study showed that the emission factors for mercury ranged from 2 to 22 lb Hg/10^{12} Btu. The one plant tested that fired a North Dakota lignite was from Unit 1 of the Creek Station and reported average was about 9 lb Hg/10^{12} Btu. The results from this test agreed very well with those results.

4.4 Mercury Balance

The mercury balance is determined by comparing the rate of mercury entering the plant to the rate of mercury leaving the plant. The various sources resulting in mercury entering Unit 2 and those resulting in mercury leaving Unit 2 are shown in Table 4-6. All the mercury balance data are expressed in units of lb/min. To express the data on the same basis, all flue gas flow rates were calculated on a moisture-free and 3% oxygen basis. The fuel feed rate was also calculated on a dry basis. The rate of mercury entering the plant via the coal averaged 9.0×10^{-4} lb/min for the 3 days of sampling. The other two sources, lime and makeup water, were insignificant in determining the mercury balance.

TABLE 4-6

Sources of Mercury for Determining the Mercury Balance

Source of Mercury to the Plant	**Source of Mercury Exiting the Plant**
Coal	Stack Gas
Lime	Fly Ash
Makeup Water	Scrubber Blowdown

To calculate the rate of mercury leaving with the ESP ash, the ash removal rate had to first be measured. The ESP inlet and outlet dust loading were previously shown in Table 2-2. Given the flue gas flow rate, the ash removal rate for the ESP averaged 665 lb/min. As stated earlier, the mercury concentration in the fly ash was very low (below detection limits); therefore, by convention (for mercury balance purposes) half the lower limit of quantification is used, in this case 0.005 μg/g. This results in a mercury removal rate in the ESP hopper ash of 8.41×10^{-10} lb/min mercury. This value is insignificant in determining the mercury balance.

Knowing the flow rates of the FGD slurry and the mercury concentration in each of the solutions (shown in Table 4-2) allowed the rate of mercury removal from the flue gas stream by the FGD system to be calculated. However, the rate of mercury leaving with the scrubber blowdown was difficult to accurately calculate. The blowdown is controlled by the level of water in the scrubber module, suspended solids, and pH of the liquor. The actual flow rate was not directly measured because it was not continuous and occurred several times during a day. Therefore, several assumptions were made to estimate the rate of scrubber blowdown. These included the average volume of FGD liquor expelled and the number of times during the day in which this occurred. On the basis of discussion with plant personnel and the measured level of suspended solids, it was estimated that the scrubber blowdown was 40 gal/min. Also, the flow rate of the unreacted slurry was assumed to be at steady state and therefore this flow rate was the same as the blowdown rate. The flow rate of mercury in the FGD slurry is shown in Table 4-7.

TABLE 4-7

Mercury Flow Rate in FGD Slurries

Day	Solid, lb/min	Liquid, lb/min
Reacted Slurry	0.82×10^{-4}	$<0.001 \times 10^{-4}$
	0.74×10^{-4}	$<0.001 \times 10^{-4}$
Unreacted Slurry	0.002×10^{-4}	$<0.001 \times 10^{-4}$
	0.001×10^{-4}	$<0.001 \times 10^{-4}$

The mercury flow rates in the flue gas were determined using the measured mercury flue gas concentration shown in Table 4-8. The mercury flow rates at the ESP inlet, ESP outlet/FGD inlet, and at the stack were calculated directly from the measured mercury concentration. Because the only sampling ports at the FGD outlet were located prior to the bypassed flue gas being reintroduced to the system, it was necessary to know the percentage of the flue gas bypassing the FGD. Unfortunately, this was not directly measured at the plant. The bypass flow rate is a function of the need for flue gas reheat and the outlet SO_2 concentration required to be in compliance with EPA requirements. The bypass flow rate, however, can be calculated using an energy balance. Using this method, the calculated bypass was approximately 55%. It should be noted, however, that the enthalpy balance was very sensitive to the gas temperature and flue gas moisture content.

TABLE 4-8

Mercury Flow Rate in Flue Gas Streams

Sample Location	Hg Flow Rate, lb/min
ESP Inlet	8.41×10^{-4}
ESP Outlet	8.21×10^{-4}
FGD Inlet*	3.69×10^{-4}
FGD Outlet*	2.91×10^{-4}
Stack	7.89×10^{-4}

* Calculated based on 55% bypass of the FGD.

The inlet sources of mercury to the plant were the coal and makeup water for the scrubber and ash sluice system. The mercury flow rate from the coal was 9.0×10^{-4} lb/min, and the total amount of mercury in the water used for makeup purposes and in the fresh lime slurry was $<0.01 \times 10^{-4}$.

The measured mercury leaving the plant was as follows:

- 7.89×10^{-4} lb/min with the flue gas
- $<0.01 \times 10^{-4}$ lb/min with the fly ash
- 0.77×10^{-4} lb/min with the blowdown solids
- $<0.01 \times 10^{-4}$ lb/min with the blowdown water

This gave a total mercury flow leaving the plant of 8.66×10^{-4} lb/min or an overall mercury balance (inlet/outlet) of 96.1%.

The mercury balances across the ESP and FGD systems are shown in Tables 4-9 and 4-10. All the mercury balances were excellent ($< \pm 5\%$). The speciated mercury balance across the FGD system also provide a reasonable balance. Based on the mercury concentrations of Hg^{2+}, the calculated removal rate of Hg^{2+} across the scrubber was 0.93×10^{-4} lb/min. The measured removal rate in the scrubber blowdown was 0.77×10^{-4} lb/min, giving a Hg^{2+} balance of 82.8%. This a good balance considering the uncertainty in the scrubber blowdown flow rate.

TABLE 4-9

Mercury Balance across ESP

	Mercury Flow Rate, 10^{-4} lb/min
Hg at the Inlet to ESP	8.41
Hg at the Outlet to ESP	8.21
Hg in the Hopper Ash	<0.01
Outlet/Inlet Balance	97.7%

TABLE 4-10

Mercury Balance across FGD System.

Location*	Mercury Flow Rate, 10^{-4} lb/min
Hg at FGD Inlet	3.69
Hg in Lime Slurry	<0.01
Hg at FGD Outlet	2.91
Hg in Blowdown	0.77
Outlet/Inlet Balance	99.7%

*Hg flow rates are based on 45% of the flow going to the FGD system.

4.5 Mercury Stability in Fly Ash

It appears that the mercury captured across the scrubber is very much associated with the solid portion of the reacted FGD slurry. After the slurry sample was taken, the sample was filtered and the concentration of mercury was measured in both the solid and liquid portions. The concentration of mercury measured in the water portion was less than 0.02% of the total mercury in the slurry.

5.0 CONCLUSIONS

On the basis of the results from the sampling program at the Coal Creek Station, the following conclusions can be made:

- The mercury emitted at stack was about 15% Hg^{2+} and 85% Hg^0.

- No mercury was captured by the ESP or on the filters of the sampling train.

- About 20% of the Hg^0 measured at the ESP inlet was converted to Hg^{2+} across the ESP.

- The FGD system removed almost all the Hg^{2+} but little if any Hg^0. The Hg^{2+} present in the stack gas was due to the flue gas bypassing the FGD.

- At the high temperatures encountered at the inlet to the air preheater, more of the mercury was measured as Hg^0 but not all of it (~95%).

- The Semtech Hg 2000 gave total mercury results highly comparable to those obtained using the Ontario Hydro mercury speciation sampling method.

- The mercury emission factor for Unit 2 was 8.57 ± 1.01 lb/10^{12} Btu.

- The mercury balance across Unit 2 was excellent, at 96.1%.

- Good mercury balances were obtained around the ESP and FGD systems for both test conditions.

- Mercury captured by the scrubber sludge was associated with the solids.

- The mercury levels in the ash sluice water and ash pond water were very low, at or near the detection limits of the CVAA.

- The chloride concentration in the flue gas was very low as is the case with all western coals. It was measured at < 1 ppm.

6.0 REFERENCES

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